ISSN 1063-7850, Technical Physics Letters, 2014, Vol. 40, No. 9, pp. 779–782. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © Yu.V. Shevtsov, B.M. Kuchumov, V.N. Kruchinin, E.V. Spesivtsev, I.F. Golovnev, I.K. Igumenov, 2014, published in Pis'ma v Zhurnal Tekhnicheskoi Fiziki, 2014, Vol. 40, No. 18, pp. 8–15.

Contactless Transfer of Image via the Gas Phase in a Thermoactivated Process

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Received April 23, 2014

Abstract—The formation of hafnium oxide (HfO_2) layers in slit structures by pulsed metalorganic chemical-vapor deposition (MOCVD) method with discrete dosage of reactants has been studied. The MOCVD process employed hafnium tetrakisdipivaloylmethanate as a precursor and oxygen as a gaseous reactant. The slit structure was formed by a silicon plate and a glass substrate with a chromium-film pattern. The slit width was varied within 0.1–2.0 mm, so that the aspect ratio changed from 150 to 30. The deposited layers were studied by the scanning ellipsometry technique. The phenomenon of image transfer from the glass substrate to the opposite plate in the form of a nanosized HfO_2 film relief, which reproduces the chromium-film pattern, is discovered. The in-plane resolution of the obtained image in these experiments reached 0.025 mm. This effect can be used for nonlithographic formation of images of film structures.

DOI: 10.1134/S1063785014090284

Artificial ordered microsystems—e.g., of the types created by MEMS and LIGA technologies, etc.—are finding increasing use in modern advanced industries. In some cases, the fabrication of these microsystems requires applying functional nanodimensional coatings onto a developed microrelief containing slits, channels, and wells with high aspect (width/length) ratios up to 1 : 1000 [1, 2].

The present work was aimed at studying specific features of the deposition of nanosized metal oxide layers in a slit system with a high aspect ratio.

Layers of hafnium oxide (HfO_2) were formed by the method of pulsed metalorganic chemical-vapor deposition (MOCVD) employing discrete dosage of reactants without a carrier gas. Volatile hafnium tetrakisdipivaloylmethanate $Hf(thd)_4$ (where thd = $(CH3)_3CCOCHCOCC(CH_3)_3$) was used as a metalorganic precursor and oxygen was a gaseous reactant. The MOCVD apparatus has been described in detail elsewhere [3]. The substrate temperature during hafnium-oxide-layer growth was maintained at 750 ± 2 K, while the $Hf(thd)_4$ vapor-source temperature was 500 ± 2 K, which corresponded to a partial vapor pressure of 212.8 Pa. The oxide-layer growth was carried out under conditions of discrete oxygen dosage by admission to an initial pressure of 2×10^3 Pa in the reactor chamber. The residual gas pressure in the reactor upon every cycle was 1.33 Pa. The total number of deposition cycles was the same (100) in all experiments.

The experiments with HfO_2 film deposition were performed using a slit structure formed by two parallel plates with a controlled gap width (Fig. 1a). The upper plate comprised a 2-mm-thick glass substrate with dimensions of 30 × 30 mm bearing a pattern of chromium (Cr) thin-film squares (Figs. 1a, 1b). The Cr film thickness was 25 nm. The lower plate was made of a Si(100) wafer. The slit width in experiments could be varied within 0.2–1.0 mm, so that the aspect ratio changed from 150 to 30. During the deposition of oxide layers, the Si substrate could be heated via contact with a heater.

The thickness of hafnium oxide films deposited onto silicon substrates was determined by the method of laser ellipsometry on the MIKROSKAN high-resolution scanning ellipsometer developed at the Institute of Semiconductor Physics (Novosibirsk). The ellipsometric angles were measured at a light wavelength of 632.8 nm for a beam-incidence angle of 60°. The spatial resolution in the scanning ellipsometry regime was about 10 μm.

During the formation of a hafnium-oxide layer on the lower (Si) substrate, the deposit exhibited a visible image that corresponded to the pattern of chromium film on the upper (glass) substrate (Fig. 1c). The thickness of the HfO_2 layer formed against the Cr squares was smaller than that against the gaps between squares

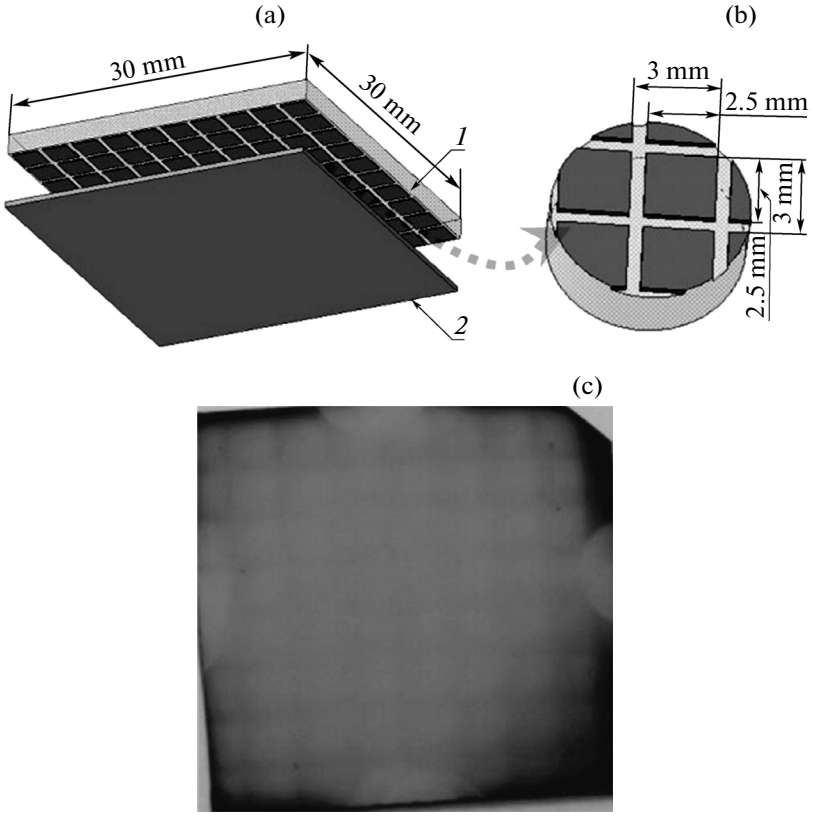

Fig. 1. Patterned oxide-layer deposition in the MOCVD system: (a) slit structure formed by (*1*) glass plate and (*2*) silicon substrate, (b) fragment of glass plate with lithographic pattern of Cr thin-film squares, and (c) photograph of the image transferred to hafnium-oxide-covered Si substrate.

(Fig. 2). We have also studied the influence of the slit width (0.2, 0.5, and 1 mm) on the contrast of transferred images. As the slit width was increased to 1 mm, the relief of the deposited film exhibited smearing. The oxide layer was also formed on the upper (glass) plate with Cr squares, but this deposit could be studied by laser interferometry in regions free of the metal because the refractive indices of the glass substrate and deposit were close. At a slit width of 0.5 mm, the obtained image resolution reached 0.1 mm.

Thus, our experiments on pulsed MOCVD with discrete dosage of reactants in a slit structure revealed the phenomenon of image transfer from one patterned plate to a parallel substrate.

In order to explain the observed phenomenon, we took into account the following peculiarities of the experiment.

(1) The observed image is formed as a result of the surface chemical reaction of decomposition of a metalorganic compound. This surface reaction (with allowance for heat supply from the substrate to the gaseous phase) is accompanied by the active generation of new components in the vapor–gas mixture, which leads to pressure variations in the near-surface layer and the related flux of reaction products from the surface to space between plates.

(2) The values of thermodynamic parameters in the system are such that the mean free path of molecules is about two orders of magnitude smaller than the slit width (i.e., the Knudsen number is on the level of 0.01).

(3) The relationship between the pressure in the reactor and the slit size is such that the time of gas flow into the slit is much shorter than the period of exposure during one MOCVD cycle.

The above limitations do not allow the observed synergetic effect of image transfer to be considered using standard approaches and approximations such as the models of (i) ultrararefied gas, (ii) continuous medium, and (iii) convective flows and the theory of Bénard convection instability. In view of these limitations, it was necessary to carry out theoretical analysis of the observed physical phenomenon using a mathematical model with a minimum set of phenomenological assumptions. It was found that the most acceptable approach was offered by the method of molecular dynamics with the potentials of intermolecular interaction and molecule–substrate surface interaction determined by quantum-mechanical calculations.

The system geometry was modeled by two coaxial disks of the same radius R_2, occurring in a cylindrical reactor of radius R_1 ($R_2 < R_1$) and height H. The inter-

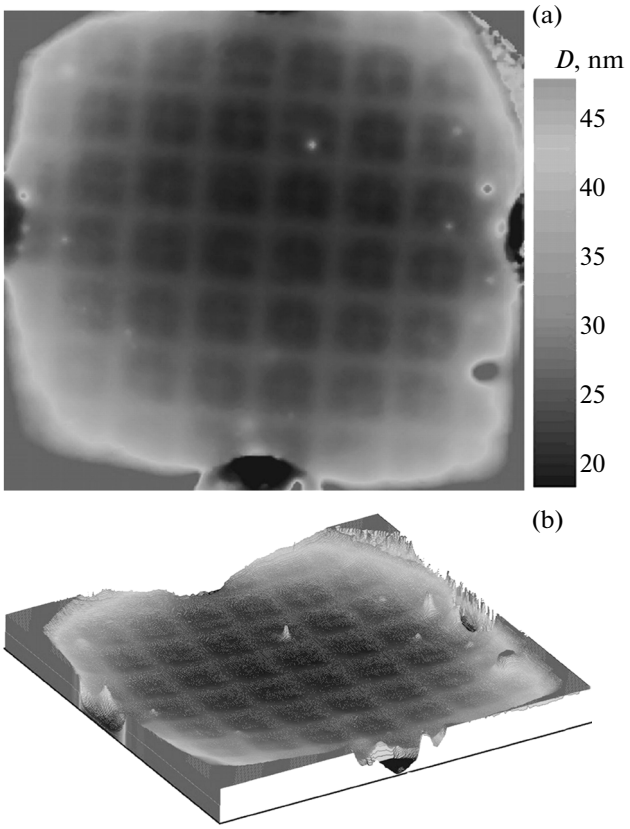

Fig. 2. Relief of HfO_2 film on Si substrate by data of scanning ellipsometry: (a) flat image (with gray-tint scale of heights); (b) three-dimensional relief.

action of molecules was described using a model of spheres wit radius *r,* interacting according to the Lennard-Jones potential with parameters $d_{LJ} = 3.405$ Å and $e_{LJ} = 1.65 \times 10^{-14}$ erg. The interaction of molecules with the surfaces of disks and reactor walls was described by the Lennard-Jones potential branch corresponding to repulsion.

The flow of molecules in the slit at constant gasdynamic parameters (corresponding to experimental conditions) in the reactor was simulated as follows. At the initial moment of time, the positions and velocities (momenta) of molecules in the ring-shaped space from R_1 to R_2 were set with the aid of a random number generator. The spatial arrangement of molecules was uniform, while the momenta were distributed according to the Maxwell law for gas temperature T_g. The number of molecules was determined in accordance with a simple ideal gas model. The system was allowed to evolve by itself with the molecules moving according to the laws of classical mechanics. Molecular trajectories in time were calculated using the classical equations of motion. As soon as a molecule fell in the space between disks (i.e., was lost from the reactor), new molecules were injected into the reactor with the aid of a random number generator so as to satisfy two conditions: (i) the total number of molecules in the system must be below theoretical and (ii) the number of molecules in the reactor must be below theoretical. If the total number of molecules in the system is equal to theoretical, the injection ceases and the number of molecules in the reactor and between disks exhibits fluctuational variation. The energy exchange with the surface of the reactor and disks was simulated using the method described in [4]. The main parameters of this energy exchange include the probability of elastic scattering on the surface (W_e) and the probability of scattering with heat transfer (W_t). In the absence of chemical reactions, these quantities must obey the condition $W_e + W_t = 1$.

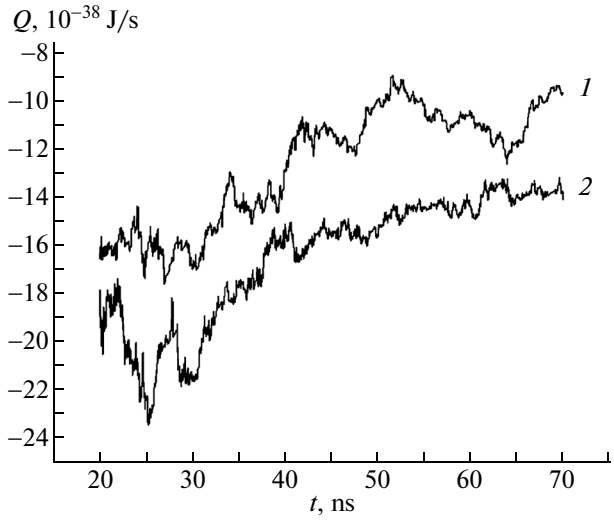

Fig. 3. Temporal variation of heat flux Q to the center of the lower disk calculated for two sets of the probabilities of heat transfer to the surface: (*1*) $W_e = 0.1$, $W_t = 0.9$ and (*2*) $W_e = 0.99$, $W_t = 0.01$.

Analysis of the gas concentration and temperature between disks was performed as follows. A set of disk radii was introduced such that the concentric rings between these radii had equal areas (and the corresponding mesocells between disks had equal volumes). Then, the state of gas in these mesocells was analyzed at certain time steps by determining the numbers of molecules in these mesoscopic volumes, their temperatures, and the fluxes of molecules and energy to the surface of mesoscopic rings on the upper and lower disks. In addition, the fluxes of momentum component perpendicular to the surface was determined, which allowed the pressure on the surface of the reactor and mesoscopic rings to be calculated.

Figure 3 shows typical results of calculations of the heat flux to mesoscopic rings on the upper and lower disks for two sets of the probabilities of heat transfer to the surface: (1) $W_e = 0.1$ and $W_t = 0.9$ (for the entire surface of the reactor and disks) and (2) $W_e = 0.01$ and $W_t = 0.99$ (in the central part of the upper disk, which models the properties of Cr coating) and $W_e = 0.99$ and $W_t = 0.01$ on the rest of the surface (and the prob-

ability of heat exchange in the reactor being the same as in the first case). The distribution of temperatures in the system was as described above.

The results of model calculations showed that the probabilities of heat exchange between molecules and the surface influence the heat flux to mesoscopic rings on the lower disk, which, in turn, affects the rate of surface reactions and, hence, the amount of a deposited reaction product, thus determining the image transfer from the upper to lower disk.

Thus, it was established that the intense heat and mass transfer under strongly nonequilibrium conditions in the gas phase during a pulsed MOCVD process in slit structures results in the phenomenon of a synergetic transfer of images from one plate to the opposite substrate, which proceeds according to a previously unknown mechanism. Direct modeling by the method of molecular dynamics revealed an asymmetry of heat fluxes in the system that depends on the thermal conductivity and temperature diffusivity of the upper disk material, which is evidence of the validity of the adopted theoretical approach to explanation of the observed phenomenon. The obtained results determine the direction of subsequent simulations, which must take into account chemical reactions involved in oxide-layer formation.

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Translated by P. Pozdeev